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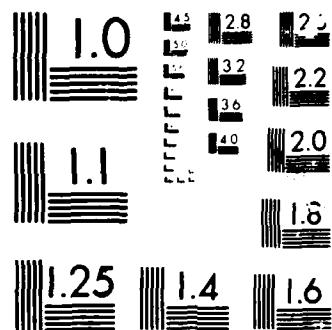
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A New Method for Analyzing Thin Side Wall Inhibitor Layers

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Abstract

Etch inhibitor layers are key to anisotropy for a number of dry etch processes, yet little is known about these layers because of the difficulty in analyzing them on the side walls where they form. In this paper we will show that an Al grid suspended above an etching surface can be used to suppress ion bombardment and allow the inhibitor to form on large horizontal surfaces which can be easily analyzed. The effect of ion bombardment on the nature of the inhibitor layer can also be elucidated using this technique. In conjunction with X-ray Photoelectron Spectroscopy, this method was used to look at the polymeric inhibitor formed during Si etching in SF_6/C_2ClF_5 with and without the presence of photoresist.

Introduction

The discharge that is struck during plasma etching is a complex environment containing a myriad of chemical species. Some of these species can undergo polymerization reactions leading to the formation of polymeric residues on surfaces exposed to the discharge. These residues play an important role in the etch process. They may affect subsequent processing steps and may require additional steps for their removal. Often, they are responsible for obtaining good selectivities. Finally, they may act as inhibitor layers, reducing the etch rate. These inhibitor layers are removed, or are modified by, ions that always bombard

any surface exposed to the discharge. The ion flux is directed normally onto the surface so that residues that form on horizontal surfaces are removed, whereas those that form on sidewalls are little affected. This interaction between ion bombardment and the inhibitor layers leads to anisotropic etch profiles, as illustrated in Fig 1.

Despite the widespread use of sidewall layers for anisotropic etching of poly-Si(1), silicides and aluminum(2), little is known about their properties. In most cases these layers are believed to be composed of halocarbon polymers because their effect on lateral etching is only seen when there is a high carbon to halogen ratio in the source gas, and increases in the carbon to halogen ratio lead to polymer formation on all surfaces. Coburn(3) has suggested that for the case of silicon etching in a mixed halocarbon gas, a thin film of fluoropolymer (a few monolayers thick) could retard the etch rate by lowering the reaction probability of the etching species. Inorganic sidewall layers may also be important in that anisotropic etching of silicon has been reported(4) in gas mixtures of SF_6/O_2 at 150 mT with no carbon sources present.

The importance of residues in the etch process requires that they be better understood. Further, the effect of ion bombardment on the nature of these residues needs elucidation. This paper describes a technique that may be used to study the effect of ion bombardment on the residues. One of the problems in analyzing the residues is that they are often present only as a thin film on sidewalls, ion bombardment having cleared the horizontal surfaces which are more accessible to analysis. The technique described here, called the 'grid technique', allows sufficient residue to form on horizontal surfaces for analysis to be feasible.

The grid technique basically involves local suppression of ion bombardment by a grid suspended some distance above the wafer; the flux of neutrals is assumed not to be affected. This would enable the simulation on horizontal surfaces of conditions that prevail on sidewalls. Following the application of this technique, x-ray photoelectron spectroscopy (XPS) was used to analyze the residue.

Ion Suppression

In a glow discharge, the mean thermal velocity of the electrons is several orders of magnitude higher than that of ions. This would result in more electrons than ions being lost to surfaces exposed to the discharge. Hence to sustain itself, the discharge has to be at a potential higher than that of any surface in contact with it. Most of the potential drop between the discharge and the surface occurs in a layer adjacent to the surface known as the 'sheath'. The electric field in the sheath forms a barrier to electrons flowing out of the plasma. These fields accelerate the positive ions coming out of the plasma, and are thus responsible for the energetic ion bombardment of the wafer surface. This acceleration process is in competition with ion-neutral collisions. Ordinarily the sheath thickness is \leq than the ion mean free path (λ_m) between collisions. Thus most of

the ions make it across the sheath without any collisions and receive the maximum energy from the sheath, corresponding to the potential drop across it.

In the grid technique, a metal grid at the same potential as the wafer is placed above the latter at a distance L , as shown in Fig. 2. The region between the grid and the wafer is field-free since they are both at the same potential. A sheath develops between the discharge and the grid, as it does at any discharge-surface interface. Ions from the discharge are accelerated across the sheath towards the grid. Those that make it through the grid enter the field-free region and are not accelerated further. The total distance the ions have to travel from the time they enter the sheath to the time they hit the wafer is several mean free paths; this results in their suffering several collisions and getting thermalized. Hence the wafer surface does not experience energetic ion bombardment but merely a flux of ions of thermal energy.

The criteria for choosing a grid for suppressing ion bombardment is that it be non-reactive with the etch chemistry, that it be fine enough to be the terminating surface for all the electric field lines in the sheath and that it be open enough not to significantly reduce the reactive neutral flux onto the wafer. For fluorine based chemistries, bare aluminum which has been plasma conditioned in a fluorine plasma is a good choice for the grid material, while for chlorine based chemistries, an oxide coated aluminum grid might be best. The grid opening should be near equal to the expected sheath thickness to terminate the sheath field and yet not restrict the neutrals.

Silicon Etching in SF_6/C_2ClF_5

The experiment to be reported in this paper is based on previous work (5) on silicon etching by this group which will be summarized in this section. The etching of silicon in a 50:50 mixture of SF_6/C_2ClF_5 is on the threshold of apparent sidewall inhibitor formation in that the etch profile is nearly isotropic when a oxide mask is used and is nearly anisotropic when a resist mask is used. This effect is shown in Fig. 3 for two wafers etched at the same time in a batch etcher. It was also reported that the range of the apparent polymer precursors was about 2.7 cm as shown in Fig. 4. This figure shows an experiment in which a narrow region near one edge of an oxide patterned wafer (see inset) was coated with resist before etching in the same SF_6/C_2ClF_5 mixture for 20 min. The results were that the etch depth was uniform across the wafer, while the undercut rapidly increased as the distance from the resist increased until it saturated at a value equal to the etch depth at a distance of 2.7 cm from the resist.

An explanation of this etch process is that the SF_6 is supplying free F which is responsible for the chemical etching of the silicon. The C_2ClF_5 is supplying some polymer precursors in the form of CF and CF_2 , but their concentration is too low to form a sufficient sidewall layer to block the F etching. When the resist is introduced, the erosion of the resist by the ion bombardment and by the free

fluorine acts as an additional source of CF and CF_2 , and now the sidewall layer is sufficient to block the lateral etching.

This etch process is of interest for evaluating the usefulness of the grid technique because it offers the opportunity of locally controlling the polymer precursor concentration at the same time as the ion bombardment is locally controlled by the use of a grid. Most of the internal plasma etch parameters can be held near constant, and samples can be etched at the same time with different ion bombardment fluxes and different polymer precursor concentrations. A key assumption for evaluating the experimental results will be that the free fluorine concentration was the same for all the samples. This assumption depends on the grid and the resist not significantly affecting the fluorine concentration. In the case of the resist, the uniform etch depth for the two wafers shown in Fig. 2, and across the wafer in Fig. 3, indicates that the resist had little effect on the free F concentration over the wafers.

Experiment

The silicon samples were etched at the same time in a batch etcher with and without a grid, and with and without the presence of photoresist nearby. Figure 5 shows the experimental configuration used. As shown, a 0.8 mm thick aluminum plate was placed over each of the silicon wafers to set the separation of the grid from the wafer surface. The plates had a number of 6mm square holes to allow etching of the wafer in these regions. When photoresist was present, it covered the surface of the Al plates exposed to the discharge. Over two of the holes on each plate, an aluminum screen (0.25mm wire on 1.4mm centers) was placed to form the ion suppression grid. Both the Al electrode and the grid/plate assemblies were grounded. One of the grid/plate assemblies was coated with photoresist on its top surface while the other plate was left bare.

The etch conditions were: plasma mode, a gas flow of 150 sccm each of SF_6 and C_2ClF_6 , a pressure of 150 mT, an etch time of 20 minutes, a RF power of 0.4 watts/cm² at 13.56 Mhz, and a electrode spacing of 3 cm. Assuming a mean collision cross-section of $6.1 \times 10^{-15}\text{cm}^2$, the ion mean free path in the collision space should be 0.33 mm. Allowing for the thickness of the screen, L should be 1.2 mm or 3.6 mean free paths. The wafers were 3" <100> p-type silicon with a resistivity of between 10 and 20 ohm-cm. The resist was Shipley 1470 and was baked at 120°C for 60 minutes after applying with a brush. Using the etch conditions above both assemblies were conditioned in a discharge for 45 minutes before inserting the wafers under the plates in order to reduce fluorine recombination on their surfaces.

After etching, the wafers were broken to prepare XPS samples, and a Dektak IIA was used to measure the etch depths as shown in Table 1. The presence of the grid alone and the resist alone decreased the etch depth by 14 and 29%, respectively. The combined grid/resist case had the greatest impact on etch

depth with a 93% reduction from the open/no resist case.

XPS Measurements

Using a Mg K_{α} x-ray source, the etched surfaces were characterized by x-ray photoelectron spectroscopy (XPS). Initial results were disappointing in that they were not repeatable and did not correlate with the etch conditions. The problem was found to be related to the air exposure of the samples between the time they were etched and the time they were loaded into the UHV system. Figure 6 shows the full XPS spectra for three exposure times (24 hrs, 2 hrs and 20 min) for open/resist samples. It is seen that the etched surfaces are affected by air exposure with the F peak totally disappearing and the O peak increasing for long air exposures. This is a limitation which strongly recommends in-situ surface analysis. However, since the samples with short air exposures (10 to 20 minutes) give distinct XPS spectra which correlated with etch conditions and which are repeatable for separate runs, the results are useful for shedding light on the properties of these inhibitor layers.

Table 2 shows the XPS peak areas and the concentration percentages from full spectra scans for the samples shown in Table 1. The air exposure was kept to a minimum (10 to 20 minutes) for these measurements. The data shown have been cross-section corrected. The Si 2p peak decreases as one goes down the table in the direction of decreasing etch rate. This suggests an increasing surface layer thickness as part of the cause for the decreasing etch depth. The total C(1s) peak does not show any significant changes. The O(1s) peak shows the same trend as the Si peak, and is consistent with a O rich region at the Si interface as discussed previously. The F(1s) peak shows the greatest change for the different etch conditions. Clearly, F is a major component in the inhibitor layer. The Cl(2p) peak tends to follow the F peak, but its concentration is at the noise level of this measurement.

Fig. 7 shows a higher resolution scan around the C 1s binding energy. We see that there is significant structure in this peak. It can be deconvolved into separate peaks using a Gaussian peak-fitting algorithm. It is well known that there is a chemical shift in the binding energy of C to higher energies as the bonding of carbon is changed from graphitic or C-H bonding to carbon-fluorine bonding. Oehrlein et al(7) has reported the binding energies for C-C, C-C-F, C-F, and C-2F bonding as 284.6, 286.9, 289.2, and 291.2 eV, respectively. Notice the variation in F content for the different samples. The residue shifts from mainly graphitic to fluorine dominated as the etch depth decreases. Table 3 shows these results in tabular form. Our peak positions agree within 0.5 eV to those reported by Oehrlein. In addition, we found a peak at 287.9 eV which Rice et al (8) assigned to C-Cl bonding.

Discussion

The etch depth results in Table 1 clearly show that the grid had the desired effect of allowing an inhibitor layer to form for the grid/resist case since there was a dramatic decrease in etch depth for this case. The XPS results show that there is a thin carbon layer, or residue, on all of the etched silicon surfaces. The residue is affected by both the ion bombardment and the presence of resist nearby. The ion bombardment appears to cause dehalogenation of the polymeric residue, leading to an increased graphitic or, possibly, unsaturated character as is clear from the carbon-to-fluorine ratios in the residue given in table 4. The polymer precursors from the resist erosion appear to increase the halogen content in the residue as is shown Fig. 7. The etch inhibitor property of the residue appears to be associated with its degree of halogenation.

Table 4 shows: a) the total surface concentration (in atom percent) of fluorine, b) the overall F to C ratio, and c) the F to C ratio in the residue. The last is given by:

$$F_C/C = (\text{Area of C-F Peak} + 2 \times \text{Area of the C-2F Peak}) / \text{Total Area of the C(1s) Spectral Envelope.}$$

In comparing the two C/F ratios, we find that much of the F in the residue layer is not bonded to C. It is likely that much of this excess F is bonded to Si and that one explanation for the inhibitor properties of these layers is that they block the desorption of the etch by-products SiF_2 and SiF_4 . As the XPS analysis has a depth sensitivity of \approx 30 to 40 \AA , the decreasing Si peak implies increasing layer thickness. The rough etch rate data indicates that the residue thickness plays an important role in etch blocking.

Conclusion

In conclusion, we have shown that a metal grid can be used to suppress ion bombardment during plasma etching and that this can be used to study the interaction between inhibitor layers and ion bombardment. Also, it can allow these layers to form in areas large enough to be easily accessible to surface analysis tools. In applying such grids to study inhibitor layer formation during the etching of silicon in $\text{SF}_6/\text{C}_2\text{ClF}_5$, it was found that the inhibitor layer was dehalogenated by ion bombardment and it appears that the dehalogenated residues are less effective in inhibiting etching.

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Table 1 Shows localized etch conditions and the resulting silicon etch depth after a single etch run for 20 min etch in $\text{SF}_6/\text{C}_2\text{ClF}_5$.

Condition	Depth (μm)	Normalized Depth
Open/No Resist	5.90	1.00
Open/Resist	5.10	0.86
Grid/No Resist	4.15	0.70
Grid/Resist	0.42	0.07

Table 2 XPS peak areas (*) and total surface concentration in atom percent for the localized etch conditions shown. Corrected for cross section.

		Si(2p)	C(2s)	Cl(2p)	O(1s)	F(1s)
Open/No Res.	*	157828	17270	---	13763	4533
	%	81.61	8.93	---	7.12	2.34
Open/Resist	*	169581	18147	2199	13836	22019
	%	75.11	8.04	0.97	6.13	9.75
Grid/No Res.	*	188371	19280	2201	13836	35598
	%	72.65	7.43	0.85	5.34	13.73
Grid/Resist	*	152395	22611	5661	10496	71639
	%	57.99	8.60	2.15	3.99	27.26

Table 3 XPS carbon 1s peak positions and percent of total carbon surface concentration for the localized etch conditions shown.

	C-C C-H	C-C-F _n	C-Cl	C-F	C-F ₂
Position ΔeV	285.0 ±0.2	286.7 ±0.6	287.9 ±0.3	289.3 ±0.3	291.7 ±0.3
Open/No Res.	75.1	11.9	----	10.2	2.9
Open/Resist	59.9	9.0	----	15.4	15.7
Grid/No Res.	38.0	19.4	2.7	17.4	22.5
Grid/Resist	16.3	6.7	4.2	31.8	41.0

Table 4 Average etch rate calculated from table 1, the total surface concentration (in atom percent) for fluorine, the atom percent of C-2F groups, the overall F to C ratio, and the F to C ratio in the residue.

Etch Rate Å/min	%F _T	F _T /C _T Ratio	F _C /C _T Ratio
2950	2.34	0.26	0.16
2548	9.75	1.20	0.47
2090	13.73	1.85	0.63
212	27.26	3.13	1.14

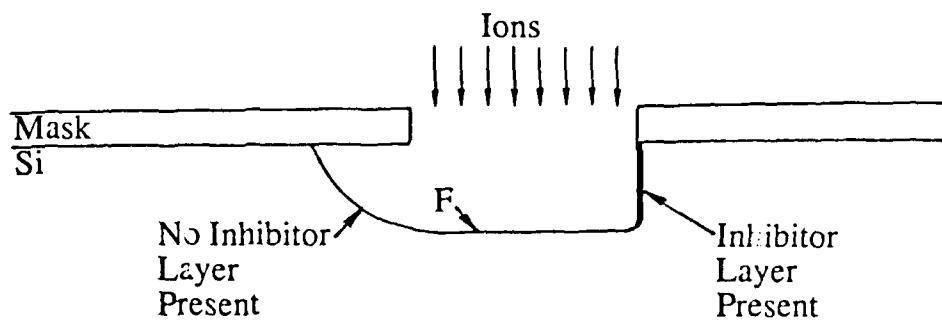


Figure 1. Cross section showing sidewall inhibitor layer blocking lateral etching.

Plasma

Sheath

Grid

Collision
space

Silicon

⊕

↓ $E \neq 0$

L

$E=0$

Ions without collisions $\propto e^{-L/\lambda_m}$

Figure 2. Sheath region showing ion collision space created by grid.



—3μm—

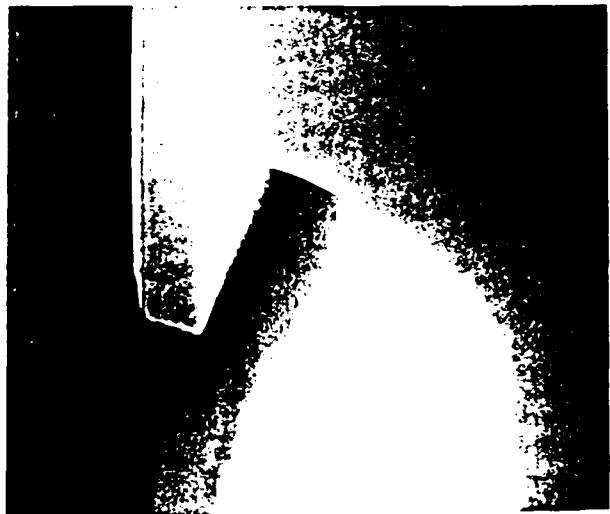


Figure 3. SEM cross sections of silicon wafer showing effect of a) oxide mask and b) oxide/resist mask on etch profile. Etch conditions: 50:50 SF₆/C₂ClF₅, 0.36 W/cm², 150 mT and plasma mode.

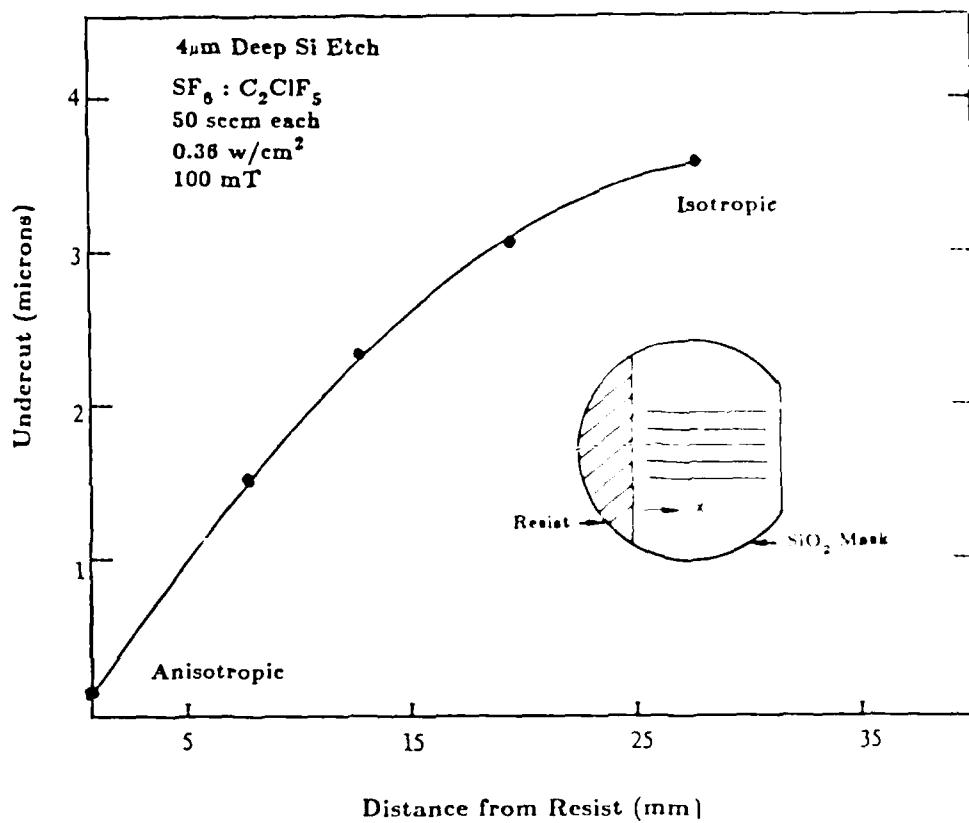


Figure 4. Experiment showing effect of resist on undercut as a function of distance from resist.

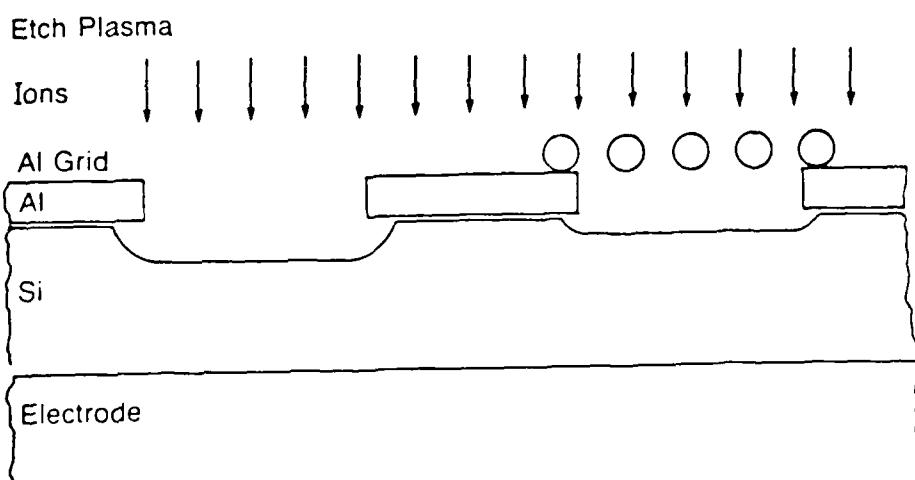


Figure 5. Plate/Gride assembly used for localized ion suppression. Resist, when used, on top side of Al plate.

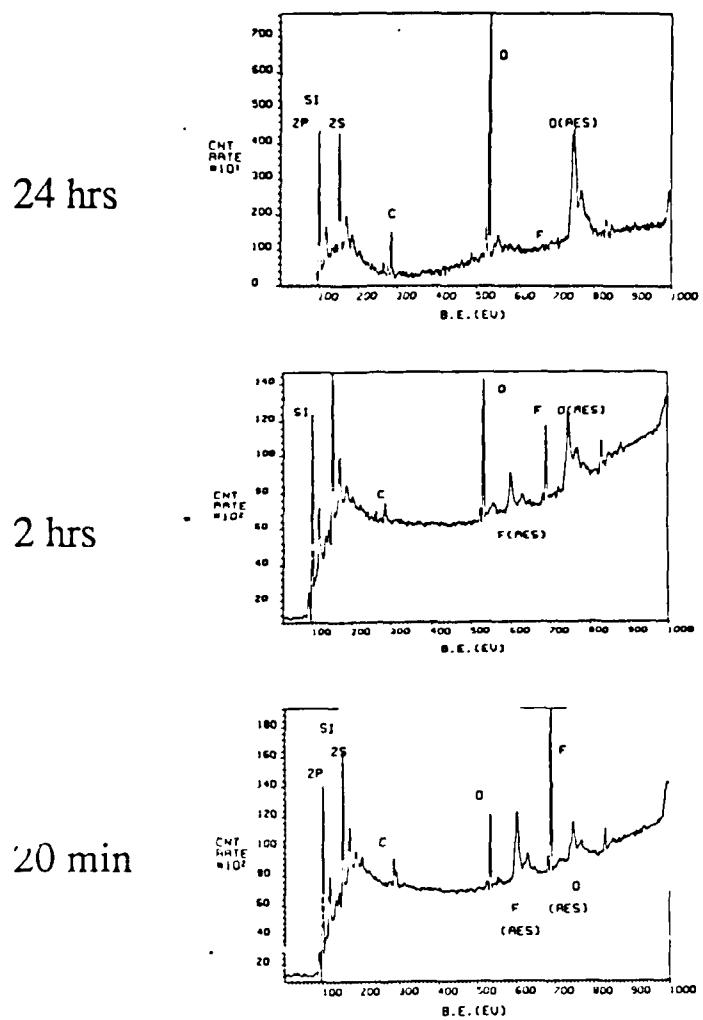


Figure 6. XPS full scan after a) 24 hrs, b) 2 hrs and c) 20 min air exposure of etched surfaces.

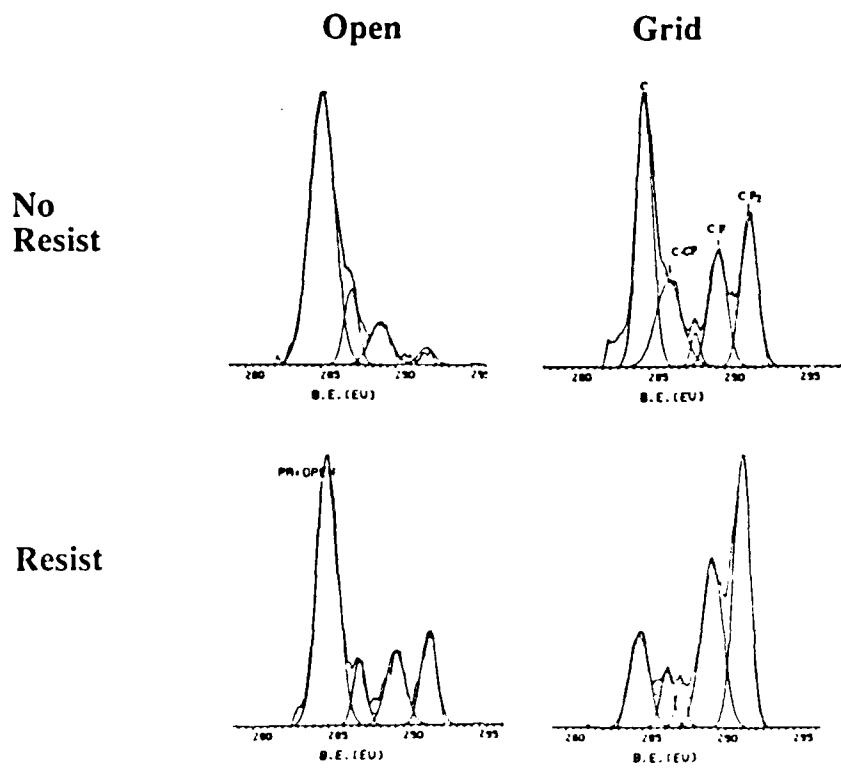


Figure 7. XPS scan of carbon 1s peaks for a) Open/No Resist, b) Grid/No Resist, c) Open/Resist and b) Grid/Resist samples.

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